Isopropenyl stearate

A new chemically bonded water repellent for paper

ABSTRACT

Paper was rapidly sized by contact with isopropenyl stearate (IPS). The use of a small amount of catalyst [0.05% p-toluenesulfonic acid monohydrate (PTSA)] and short curing times (4–15 s) at 160–190°C provided conditions for chemical incorporation of the long fatty chain at a low degree of substitution (DS < 0.001). The modified paper was repellent to boiling water and resistant to feathering by writing ink. Tensile strength and the coefficient of sliding friction were essentially unchanged. The Cobb test demonstrated low water absorptivity. Laminates with sodium silicate also exhibited desirable properties when exposed to high relative humidity and upon submersion in water.

KEYWORDS
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The papermaking industry has long sought new efficient sizing agents, especially those imparting novel, useful properties to paper. Paper has been conventionally sized either by mixing size with the aqueous pulp slurry or by coating the surface of the formed sheet. Physical adsorption or chemical reaction of the size with the cellulose hydroxyl groups may result. Examples of the former are rosin–aluminum sulfate combinations, wax, asphaltic agents, and resins or polymers intermixed with or covering the fibers. Chemical bonding to fibers has been achieved through the application of acid chlorides, anhydrides, azides, isocyanates, and certain resins (*1*). Cellulose film has been acylated directly by long exposure to the hot vapors of fatty acids (*2*).

An important advance in the early 50's was the introduction of alkyl ketene dimers as the sizing agent (*3–5*). These compounds chemically form the β-ketoester derivative of cellulose by partial reaction of surface hydroxyl groups (*5*). Treatment generally involves an emulsion of the alkyl ketene dimer and aqueous pulp slurry. After sheet formation, the paper is dried and aged 1–3 days to optimize the water repellency.

Our laboratory has developed isopropenyl esters of long-chain fatty acids as a novel class of reactive acylating agents (*6–14*). Isopropenyl esters react with hydroxyl hydrogens of cellulose in the presence of a trace of acid catalyst. For example, in representation of the cellulose reaction, the isopropenyl ester acylation of an alcohol substrate is depicted by Eq. 1.

$$\begin{array}{l} RC(=O)-O-C(CH_3)=CH_2 + R'OH \xrightarrow{H^+} \\ \qquad RC(=O)-OR' + CH_3COCH_3 \end{array} \qquad (1)$$

The acetone evolved can be recovered to meet environmental standards. The trace amount of acid catalyst is easily removed or neutralized.

The reaction is practical with long-chain isopropenyl esters, of which isopropenyl stearate (IPS) is of particular interest. These esters have long storage life in the absence of catalysts. In the absence of cellulose, acid catalysts slowly induce self reaction of the isopropenyl stearate to give stearic anhydride as one identified product in the mixture.

Because of the commercial availability of stearic acid, isopropenyl stearate (m.p., 37°C) is cost-competitive with other acylating agents (*15*); IPS is prepared by direct addition of stearic acid to propyne in the presence of zinc catalyst (*10*). Pure fatty acids are not required to form isopropenyl esters for commercial applications. For this purpose, inexpensive tallow fatty acids provide the comparable liquid isopropenyl tallowate.

Results and discussions

Isopropenyl stearate may be applied to paper either neat or by deposition from

Lot	Specimens per group sample	Curing time, s	Avg. tensile strength, kg/cm²	Water repellency[a]
		Neat melt treatment[b]		
Control[c]	9	...	88.9	None
A	9	4	82.6	Excellent
B	9	8	87.5	Excellent
C	9	12	84.0	Excellent
		Benzene deposition treatment[b,d]		
Control[c]	4	...	58.4	None
D	4	15	36.6	Excellent

[a]According to reference (22), except that excellent describes the formation of water globules without significant wet spots. [b]Curing conditions: PTSA/IPS = 0.05%–0.5%, 185°C curing temperature. [c]Untreated virgin paper. The observed data for neat melt and benzene deposition were obtained from separate lots of Whatman No. 1 nondirectional paper. [d]50% IPS in solution; PTSA/IPS = 0.05%.

an organic solvent. Neat treatment may be carried out in either of two modes—as a liquid melt containing a catalytic amount of PTSA (*p*-toluenesulfonic acid) or other suitable catalyst (e.g., β-naphthalenesulfonic or phosphoric acid) or as a powder containing the catalyst. The paper is completely covered with melt and cured by ironing or in the nip of heated rolls.

The neat mode of treatment has several advantages. Since the fibers do not swell by neat treatment, only surface acylation is afforded that results in a degree of substitution (DS) of about 10^{-3}. This corresponds to incorporation of less than 0.2% w/w of size. Direct weight determinations at these low levels of sizing are unreliable for DS calculations because of uncertainties in the moisture equilibration of treated and untreated fibers. However, micro-determination of the stearoyl group (~0.15%) in the modified papers gave a DS of 10^{-3}, in correspondence with the value found for IPS stearoylated cotton fibers (*16*). The low DS reveals that only one hydroxyl per 1000 anhydroglucose units (or one hydroxyl per 3000 hydroxyl groups) is acylated, a value that supports the conclusion that acylation is confined to the fiber surface. The amount of PTSA used to achieve acylation may vary, but the preferred concentration is 0.05%. This quantity, formerly calculated from the statistical evaluation of parameters in the IPS acylation of cotton fibers (*17*), was adopted and applied to the acylation of paper.

In an alternative treatment, an inert volatile solvent such as methylene chloride may be used for depositing a mixture of the isopropenyl ester and catalyst. The technique simply involves dipping the paper into the solution and evaporating the solvent.

The tensile strengths of neat-treated papers were essentially unchanged (Table I). Some loss of tensile strength of paper treated by the solvent-dipping procedure may have been caused by the effects of uncontrolled relative humidity (*18*). Modification by solution addition of size may be expected to reduce tensile strength, since solvent penetration of the fibers affords acylation of the fiber core which may break inter- and intramolecular hydrogen structures. Higher concentrations of acid catalyst may also cause hydrolytic change of the cellulose chain.

Surface sizing with long-chain aliphatic compounds imparts excellent water repellency despite the low degree of substitution (Table I). The Cobb test (*19*) for absorptiveness (g of water/m²) gave values of 3.98 for the felt side and 3.85 for the wire side. More severe tests with single-sheet and laminated-specimen papers further support the excellent water repellent properties. The sized paper after a 3.5-hr submersion in water appeared dry and opaque. In fact, the stability of the IPS-sized papers to boiling water is a striking feature of the protective characteristics of the sizing agent. Sized paper, after submersion in boiling water for 1200 s and shaken free of superfluous water, appeared dry and felt dry to the touch. This property afforded by IPS acylation was surprising in view of the report that ketene dimer sized paper is wetted by hot liquids (*1*).

The 5-layer laminate of modified paper (three papers interlayered with two sodium silicate coated papers) submersed in water at 21°C absorbed 8% water in 15 min and 15% water in 45 min. A 5-ply laminate of unsized paperboard became waterlogged within 45 min and became completely delaminated under the described test.

Similarly, seven-ply paperboard was prepared from unsized and from IPS-sized paper by interlaying with sodium silicate. The laminates were suspended above water in closed jars and exposed to the vapors for 72 hr at 20°C. The unsized paperboard absorbed water and was completely delaminated. The IPS-sized laminate, by contrast, held together and retained good rigidity except for the two outer plies, which became partially separated.

Paper sized with IPS showed other improved properties. The paper presented an excellent receptive surface for writing ink. Good resistance to feathering by writing with a quill pen and blue-black ink was obtained with add-on as small as 0.20% (DS = 1×10^{-3}). Attempts to write on unsized paper resulted in marked feathering. A measure of the sizing resistance to ink absorption was then determined by color comparison with similarly treated unsized control paper. Sized papers immersed for 15 s were stained by a trace of blue color compared to a dark blue color in the controls. Sized papers, after immersion for 1200 s, were stained a light blue color compared to very dark blue in the controls. The small amount of ink absorbed by the sized papers did not penetrate beyond the surface, as shown when papers were split at the thickness. In the treated paper, ink stain was absent at both interior surfaces, whereas unsized paper was stained throughout.

Paper modified with IPS afforded a very receptive surface to offset and letterpress printing inks on which the printing was sharply demarcated. In a castor oil penetration test, a stable translucent spot was obtained in an average time of 15 s.

The coefficient of sliding friction (μ) was measured because of its importance in the calender stacking of sheet paper. The coefficient was equivalent in the sized and unsized papers (μ = 0.9). This represents another improvement over ketene dimer sized paper, for which the coefficient was reduced, compared with unsized paper.

On the basis of the above physical and dynamic mechanical properties of IPS-treated paper, IPS shows considerable promise as a new chemically bonded size. It provides a hard finished permanent paper with excellent brightness and essential retention of tensile strength. A reviewer of this manuscript has suggested that "because of the higher cost and specific property requirements, the specialty papers, such as electrical insulation or condenser papers and paper clothing among others, appear to be good candidates" for this treatment. Further studies into lowering the cure temperature and into the wet-end use of the liquid isopropenyl tallowate should be undertaken to extend the utility of these unique acylating agents. Conceivably, other methods of application such as vapor phase or emulsion techniques may be useful in extending the utility of this unique size. Isopropenyl ester sized broke should be readily recyclable. The results of sapon-

ification with alkali show that this size can be completely removed (*16*).

Experimental

Materials

Isopropenyl stearate was prepared from commercial grade stearic acid [stearic acid (89%), palmitic acid (9%), and homologues (2%)] by the reported method (*10*). Two lots of Whatman No. 1 filter paper (0.018 ± 0.001 cm thick) consisted of nondirectional fibers of essentially pure α-cellulose with a basis weight of 90 g/m^2. The paper was air-equilibrated before use in all experiments. All solution concentrations were percent by weight unless otherwise indicated.

Paper treatment

Neat application of melted IPS. The paper was placed upon a Pyroceram[1] plate on insulated pads. As an example of preparing the IPS-PTSA (*p*-toluenesulfonic acid monohydrate) mixture, 50 mg (0.05%, 0.00025 mole) of PTSA was added to 100 g (0.31 mole) of melted IPS, and the mixture was swirled on a hot plate at about 100°C until a single phase formed. The filter paper was completely covered with the poured melt and cured on each side with a heated flatiron (185°C). The temperature was controlled (±5°C) with a thermocouple contained in the sole plate of the heavy iron. Since the area of the paper was approximately twice that of the sole plate, the latter was moved rapidly over the paper for double the indicated period. Each side of the paper was cured separately. The brief heat treatment did not cause visible thermal or oxidative damage to the paper. To distinguish between effects of chemical reaction and physical adsorption, unreacted material was removed with methylene chloride in a Soxhlet extractor. Other suitable solvents, such as diethyl ether or benzene, were also used to extract the unreacted IPS and acid catalyst.

Neat application of powdered IPS. Fifty mg (0.5%; 0.00025 mole) of PTSA was added to 10.0 g (0.031 mole) of melted IPS, and the mixture was swirled until homogeneous. The melt solidified upon cooling to room temperature (20–24°C). The paper was dusted with sufficient powdered solid to cover it with melt when ironed at 185°C for 15 s. The treated paper was exhaustively extracted with methylene chloride in a Soxhlet extractor to remove unreacted size and catalyst.

Solution application of IPS. Filter paper was immersed in 100 ml of benzene[2] solution containing 50 mg of PTSA and 10.0 g of IPS. The mixture was shaken for 1 min, and the paper was air-dried in a hood and cured at 185°C for 15 s with the flatiron. Unreacted sizing was extracted in the previously discussed manner.

Laminated papers. Five-ply laminates were prepared in the following manner: Five papers were sized with IPS-PTSA (0.5% PTSA) melt for 8 s at 185°C and extracted with methylene chloride in the usual manner. Two of the papers were coated on both sides with sodium silicate (41° Baumé at 21–23°C), and the excess was removed with a spatula blade. The weight increase due to sodium silicate was 250%. A five-layer laminate was prepared by sandwiching the two sodium silicate coated papers between uncoated papers and then pressing at 3.5 KPa/cm^2. The laminates were dried in an oven at 45°C for 50 min, weighed in sealed plastic bags, then tested for water repellency by submersion in a capped jar of water at 21°C. The laminates were lightly patted between blotters to remove extraneous water and weighed rapidly.

Seven-ply laminates similarly prepared were exposed to the saturated air above water in closed jars for 72 hr at 23°C.

Stability to boiling water. Sized paper from the neat application of melted IPS was submerged in boiling distilled water for 1200 s to observe its appearance after removal.

Resistance to feathering and ink absorption. A quill pen and blue-black ink were used to inscribe specimens of sized paper from the neat application of melted IPS and controls of virgin filter paper. The extent of feathering was observed; specimens treated by 15 s and 1200 s immersions in blue-black ink were rinsed in running distilled water for 5 s, and the color was observed after drying. The test specimens were then split at their thickness, and the depth of ink penetration was observed.

Printability. A variety of offset and letterpress printing inks were applied to the IPS modified filter paper. The time of penetration of a castor oil drop on a specimen paper to form a stable translucent spot was observed.

Determination of degree of substitution

A method for the determination and identification of chemically bound fatty acid present in partially esterified cellulose materials has been recently reported (*16*). The method was applied to the determination of the degree of substitution of the sized papers, defined as moles of stearoyl group per mole of anhydroglucose unit.

Physical testing procedures

Water absorptiveness by the Cobb test was determined by TAPPI Test Method T441-os-77 (*19*). Tensile strength was determined by the ASTM Standard Method D-1682-64 (1975) (*20*). The coefficient of sliding friction was measured by ASTM Standard Method D-202-77 (*21*). Water repellency was determined by AATCC Test Method 22-1971 (*22*).

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[1]Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

[2]The Occupational Safety and Health Administration, under Standard 29 CER 1910.1000 Table Z-2, has stated that benzene is a carcinogen.